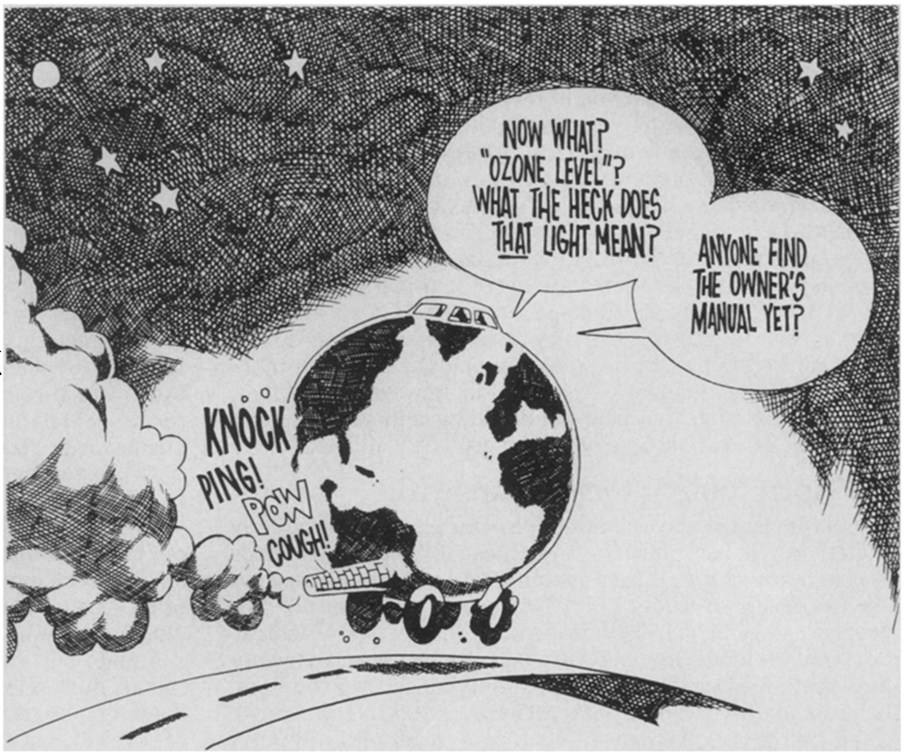
Decline of the CFC Empire

An industry is scrambling to prepare for the next decade, when the United States and other nations will have to cut their use of these ubiquitous chemicals at least in half

By RICHARD MONASTERSKY



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Over the past few decades, they have developed into the wonder chemicals of U.S. industry.

These compounds are used to make the foam cushions upon which this country sits and sleeps. Air conditioners and refrigerators rely on their special thermal properties. They fill the energy-saving foam panels that insulate buildings and almost half the new houses built in the United States each year. And they clean the printed circuit boards that run television sets, computers and the space shuttle's complex electronics.

Chlorofluorocarbons, or CFCs as they are more generally known, have permeated almost all aspects of modern life. Nontoxic, nonflammable, noncorrosive and extremely stable, they have become the chemical of choice for a myriad of industrial purposes. But while CFCs once seemed perfectly harmless, experts now regard them as a serious threat to the environment and human health. Indeed, the perceived threat is so great that chemical companies around the globe are investing tens of millions of dollars in the search for safer substitutes, and the world's largest manufacturer of CFCs two weeks ago reversed its corporate stand by announcing it would eventually end CFC production.

More than a decade ago, scientists realized that CFCs were accumulating high above the earth and consuming ozone – the all-important molecule in the stratosphere that shields life on earth from the sun's ultraviolet radiation. Later, investigators also discovered that CFCs in the atmosphere are helping to drive up the planet's temperature, contributing to the greenhouse effect.

The United States has joined 31 other nations in signing a treaty that seeks to protect ozone by forcing an immediate freeze and then a reduction in the use and production of CFCs. This agreement, known as the Montreal Protocol, calls for a 20 percent cut in CFCs by 1993 and an additional 30 percent cut in 1998.

At present, only two countries – the United States and Mexico – have ratified the Montreal Protocol. Scheduled to take effect Jan. 1, 1989, the agreement will become binding only after 11 countries, representing two-thirds of the global consumption of CFCs, have ratified it (SN: 7/26/87, p.196).

Yet even after the accord was signed last September, environmental groups continued their ever-accelerating movement to stop all production and use of ozone-destroying chemicals. These groups claim that a 50 percent cut in CFCs will not stop the weakening of the ozone layer, and their concern is buttressed by new findings about the loss of ozone.

Although the industrial world has traditionally argued against such draconian measures, Du Pont, the world's leading producer of CFCs, stunned industry two weeks ago by joining the environmental bandwagon. It announced that it will support plans to strengthen the Montreal Protocol, and called for a total worldwide ban on CFC production. Although it mentioned no specific timetable, Du Pont believes that with stronger regulations, it could complete this phaseout shortly after the turn of the century.

In early March, only three weeks before this announcement, Du Pont had said it would not support a total phaseout of all CFCs. But according to spokesperson Craig Skaggs, Du Pont reversed its position after an international panel of scientists reported on March 15 that primarily because of CFCs, the global ozone layer was disappearing at an unexpectedly fast rate (SN: 3/19/88, p.183). Between 1978 and 1985, global levels of stratospheric ozone dropped on average 2.5 percent.

This report moved the Environmental Protection Agency (EPA) last week to endorse strengthening the Montreal Protocol. An international team of experts is scheduled to reassess the protocol in 1989 using the latest scientific information, but because of the new findings EPA Director Lee M. Thomas now suggests the team meet this fall, in order to speed the process of revising the treaty.

In the United States alone, more than $135 billion worth of products rely on chlorofluorocarbons, and their precipitous fall from grace has sent the affected industries scrambling to find ways of reducing dependence on these chemicals.

Conservation has become the short-term answer as companies try to recycle or dilute CFCs. For a more permanent solution, however, chemical companies are searching for alternative compounds that will fill in for CFCs without destroying the ozone layer.

There have been significant advances within both these arenas, but no panaceas have appeared yet.

For all industries affected by CFCs, it is a race against time. "Based on what we know today, the 12-year timetable of the Montreal Protocol is very tight," says Kevin Fay, director of the Alliance for Responsible CFC Policy, an association based in Rosslyn, Va., that represents CFC users and producers from the United States.

"I think you're going to see a lot of diversity in terms of R&D and new technology. It's a real race by companies to find the most cost-effective way out of this situation."

MOST WIDELY USED CFCS AND HALONS

COMPOUND (chemical formula)	OZONE DEPLETION POTENTIAL*	ATMOSPHERIC LIFETIME (YEARS)	AMOUNT USED IN U.S. (millions of kg)	AMOUNT USED WORLDWIDE (millions of kg)	MAJOR USE
CFC 11 ($CFCl_3$)	1.0	64	79.7	368.3	rigid and flexible foams, refrigeration
CFC 12 (CF_2Cl_2)	1.0	108	136.9	455.0	air conditioning, refrigeration, rigid foam
CFC 113 ($C_2F_3Cl_3$)	0.8	88	68.5	177.0	solvent
Halon 1211 (CF_2BrCl)	3.0	25	2.8	7.1	portable fire extinguishers
Halon 1301 (CF_3Br)	10.0	110	3.5	7.0	total-flooding fire ext. systems
HCFC 22 ($HCClF_2$)	0.05	22	99.2	figures not available	air conditioning

*Ozone-depleting potentials represent the destructiveness of each compound. They are measured relative to CFC 11, which is given a value of 1.0.

Will not be limited by Montreal Protocol

Consumption data based on 1985 figures.

Source: EPA

The Montreal Protocol specifically limits five CFC compounds (11, 12, 113, 114 and 115) and three forms of another class of chemicals called halons. (Used mostly in fire extinguishers — both the hand-held versions and the large kind on aircraft carriers — halons are not consumed in nearly the same volume as CFCs, but they are more effective in destroying ozone and their production levels will be frozen at 1986 values.) Together, CFCs and halons fall under the name halocarbons.

CFCs all share a common molecular structure that includes a carbon atom surrounded by a combination of fluorine and chlorine atoms. In halons, an atom of bromine replaces some or all of the chlorine atoms.

The problem with the halocarbon arrangement is that the molecules are too stable. Able to survive for 100 years or more in the lower atmosphere, halocarbons break apart when they diffuse 20 miles up into the stratosphere and are bombarded by ultraviolet radiation. Up there, in the middle of the ozone layer, these compounds release their chlorine and bromine, which chemically attack the surrounding ozone (O_3) and convert it to molecular oxygen (O_2).

CFC producers have so far followed two paths in the search for replacement molecules. One method seeks a variation on the general CFC pattern by sticking a disruptive hydrogen atom into the stable arrangement of chlorine and fluorine. Because these new molecules are less stable, they break up in the lower atmosphere and are less liable to reach the stratosphere where they can do harm.

A second method abandons the CFC idea altogether: Chemical companies are now working on potential replacements that contain no ozone-destroying chlorine or bromine.

Already on the market are several compounds that incorporate hydrogen into their structure. One of these, HCFC 22, is used as a coolant in a growing percentage of home air conditioners. Because it contains a hydrogen atom, it is 20 times less destructive of ozone than CFC 12, which is the most widely used of the chlorofluorocarbons, appearing in most refrigerators and auto air conditioners.

Although HCFC 22 will not be limited by the Montreal Protocol, the other sections of the coolant industry—especially the automobile industry—are reluctant to make the switch to this chemical because it would require substantial changes in hardware. HCFC 22 works at a higher pressure than CFC 12, and systems using this newer chemical need much heavier compressors and stronger tubes.

Rather than adopt the currently available compound, the refrigeration and auto air conditioning industries have placed their hopes in HFC 134a, a compound that is still undergoing toxicology tests and is not expected on the market for several years, says Joseph Steed, an environmental manager in the Freon products division of Du Pont, which produces a quarter of the CFCs used around the world.

According to Steed, this chemical, which contains no chlorine or bromine, promises to be a good substitute for CFC 12 and may fit into the present cooling systems without requiring a substantial redesign.

Although Du Pont and more than a dozen other companies will be competing to market HFC 134a, an international group of 14 companies announced in January that they have banded together in an effort to speed this chemical and another, HCFC 123, through toxicology tests, which are expected to run five to seven years. The companies also will split the cost of the roughly $4 million tests.

HCFC 123 has been touted as the replacement for CFC 11, which is the second most widely used chlorofluorocarbon. In the United States, CFC 11 serves primarily as a blowing agent for foams — both the soft foam used in seat cushions and the hard foam used as insulation in buildings and refrigerators. Outside the States, the major use of CFC 11 is still as an aerosol propellant in spray cans.

While Du Pont and other U.S. producers such as Allied-Signal have traditionally hyped HCFC 123 as the next blowing agent, Pennwalt Corp. has been developing another foam-blowing compound, HCFC 141b. Although 141b is not included in the joint toxicology testing program, it is farther along in the testing process. And this chemical is produced as a by-product of another chemical operation, which means that Pennwalt already has a production line that can put out commercial quantities of 141b. "By late 1990, 1991, we believe we can go commercial with 141b," says Gene Laughlin, a market manager for Pennwalt in Philadelphia.

Recently, other U.S producers have started to investigate the potential of 141b. At this point, it is unclear which substitute chemical actually performs better, although initial tests show that neither performs as well as CFC 11.

While the agreement on the Montreal Protocol sent waves of concern throughout the entire realm of the CFC empire, none felt those waves more strongly than the electronics world, which uses CFC 113 as an all-purpose cleaner for circuit boards.

Chlorofluorocarbons first attracted the scrutiny of environmental forces more than a decade ago in a movement that brought about the ban of CFC use in aerosols in the United States and several other nations. Feeling the environmental heat at that time, chemical companies started to develop substitutes for the most widely used CFCs, numbers 11 and 12. Therefore, those who use 11 and 12 – the foam and refrigeration industries – have long known that potential substitutes were sitting on the horizon.

But the widespread use of CFC 113 postdates the environmental concern of a decade ago, and it is only recently that negotiators have pressed for a ban on CFC 113 along with the others.

"CFC 113 was not even an issue until two years ago," says a public policy specialist who works for a large electronics manufacturer. "So we are well behind those other two industries."

Although it appeared that there was no real substitute available for CFC 113 at the time of the Montreal Protocol, industry members were heartened in January by the announcement that a currently available compound, called BIOACT EC-7, is showing promise as a partial replacement for CFC 113.

EC-7 was born three years ago, when a small company in Fernandina Beach, Fla., called Petroferm, Inc., isolated an organic solvent from orange peels. The chemical fits into a class known as terpines and is very similar to kerosene or turpentine. According to Craig Hood of Petroferm, EC-7 cleans soldering residue off printed circuit boards "as well as or better than CFCs."

As part of an agreement with Petroferm, American Telegraph and Telephone Co. has been testing the new solvent for the last three years and anticipates it can substitute EC-7 for up to 30 percent of the 15 million pounds of CFCs it uses each year, says John Fisher of the AT&T Engineering Research Center in Princeton, N.J.

EC-7 may be able to replace a sizable share of the CFC 113 market, but the new chemical has its limitations because it is not as versatile a cleaner as the chlorofluorocarbon. Moreover, it is flammable and therefore presents a hazard electronic companies did not need to address when they used CFC 113.

Industry representatives have called the new compound "a promising chemical, but not a magic one." The industry is still searching for other substitute chemicals. Yet it's clear, say the representatives, that no compound will be able to replace CFC 113 across-the-board.

According to EPA estimates, industry consumed 2.5 billion pounds of CFCs and halons worldwide in 1986, which amounts to slightly more than a half of a pound for every person on the globe. In the same year, the United States used over 700 million lb, almost 3 lb per capita.

If CFC consumption were allowed to skyrocket at its present rate of growth, the United States would be using almost 800 million lb of these chemicals by 1990, and over 1 billion lb by the year 2000. However, if the protocol advances according to plan, the U.S. consumption in 1993 would drop to approximately 600 million lb. By 1998, when the second phase of the reductions begins, that figure should dip to around 350 million lb.

It is difficult to tell at this point whether the substitutes will be ready before one or both of those reductions go into effect. Fortunately, though, the industries do not have to wait for substitutes to hit the market; many are now in the process of cutting back on their CFC use through recycling.

In the electronics industry, for example, 85 percent of chlorofluorocarbons used in cleaning circuit boards immediately enter the atmosphere. That amounts to over 330 million lb a year worldwide, according to EPA figures.

"There's no question but that if we spend the money, we can design systems that will capture the CFCs and allow us to reuse them," says Jim Rogers at Digital Corporation, an electronics manufacturer in Stow, Mass.

The coolant industry can also conserve by making simple changes. Until now, a standard test for air conditioners has been to pump up the system with chlorofluorocarbons and then wait to see if any of the coolant leaks out – a process that sends the volatile CFCs right into the atmosphere. However, mechanics should be able to use some other substance for these tests, says Fay. In addition, it may become common practice to remove the coolant from air conditioners and refrigerators before they are crushed at the junkyard.

Halons are proving far more difficult to replace than CFCs. Chemical companies discovered these chemicals by trial and error, and they are just now exploring the chemistry behind the halons' fire-extinguishing abilities, says Capt. E. Thomas Morehouse Jr. of the Fire Technology Research Branch at Tyndall Air Force Base in Florida.

While there are no prospective substitutes for halons, the use of these chemicals will drop enormously with a redesign of firefighting equipment and a change in testing practices. Because they are nontoxic, liquid halons are ideal for use in buildings, aircraft, ships and other areas that are filled with people. Yet these chemicals are released far more frequently during tests than during fires.

Halons also evaporate quickly without leaving a residue, which makes them a favorite for putting out fires at facilities that hold valuable materials, such as computer centers and rare-book libraries. In the past, it has been customary to use a firefighting system that floods a burning room with 500 lb of halon 1301, the halon most destructive of ozone. But new systems are available that are mounted on computer casings and contain only 2 lb of a much less destructive halon, says Steve Anderson of the EPA.

As another short-term tactic, the electronics industry is developing diluted blends of CFCs that allow customers to use smaller volumes of these chemicals.

Currently, one of the most widely used solvents is a Du Pont blend called Freon TM that contains 94.3 percent CFC 113 and 5.7 percent methanol. This mixture, called an azeotrope, is special because its chemical components act as a single substance during boiling.

The properties of an azeotrope depend critically on the proportions. A mix of 90 percent CFC 113 and methanol, for instance, would separate when boiled because the methanol and CFC have different boiling points.

Two months ago, Du Pont announced it had discovered a new azeotrope that contains only 67 percent CFC 113, as well as methanol and trans-1,2-dichloroethylene. Called Freon SMT, this compound is a better cleaner than Freon TM, according to Mark Wolff of the Du Pont electronics department. Moreover, it is only 75 percent as destructive to ozone as the older azeotrope.

Time and money. Several years and billions of dollars are standing in the way of society's complete adjustment to life without CFCs. It will cost the U.S. economy approximately $5.5 billion between 1990 and 2010 to make the transition, according to calculations by the CFC Alliance. Through the year 2075, the EPA projects that this figure will rise to $27 billion.

But the price is insignificant when compared with the EPA projections for the cost of skin cancer deaths that would result if countries did not enact ozone-protecting measures. According to EPA's Stephen Seidel, the increased amount of ultraviolet radiation would kill 3 million people either alive today or born before 2075. In monetary terms, the health benefits of the Montreal Protocol would amount to a U.S. savings of almost $6.5 trillion by 2075.

The protocol may be only the beginning. If the recent announcements by Du Pont and the EPA are any indication of the world's political and environmental climate, the treaty nations might soon be moving toward a total ban.

Even with a total phaseout, though, the damage to the ozone layer cannot be healed overnight. The scientific projections are not clear, but some calculations suggest that high chlorine levels in the stratosphere will persist until the 22nd century or later. □